

Coating agent for protecting ceramics or glass against thermal oxidation comprises a phosphorous silicate nanosol which is a hydrolysis product of metal alkoxides or metal halides and acidic organophosphate solution

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Abstract of DE19929616

Coating agent comprises a phosphorous silicate nanosol which is a hydrolysis product of metal alkoxides or metal halides and an acidic organophosphate solution. An Independent claim is also included for a process for the production of a transparent coating comprising producing an acidic organophosphate precursor solution (I); producing an acidic phosphorus silicate nanosol (II) by mixing (I) with metal oxides or metal halide sols or their precursors; coating the substrate with the nanosol; drying the coating to form a gel layer; and heat treating the gel layer at at least 440 deg C.

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The invention relates to means to the contactor of metal surfaces before thermal oxidation and a transparent coating to the contactor before thermal oxidation, formed with such means. The coating layer becomes preferred the contactor of metals, in particular ferrous metals, aluminium, copper or their alloys, used.

It is known that metal surfaces (z. B. Ferrous metals) with elevated temperatures in atmospheric environment rapid oxidized become. Visible features of the oxidative attack at ferrous metals under these conditions are discolorations of the surface by thin films of the oxidation products of the metal (approach and tempering colors), which the performance characteristics of the Metals considerable limit.

For the contactor before corrosion by thermal oxidation current different methods are used, in particular:

(1) Painting procedure (z. B. EP 0813473 A, US 5554681).

These can become in the temperature range starting from 300 DEG C only briefly used. The thermal decomposition (pyrolytic cracking) of the bonding agent prevents higher application temperatures.

(2) Galvanic one (z. B. Eloxal and Emetal method) and pickling procedure (z. B. DE 197 40 248 A1, ALODINE method Parker Amchem, bond he and Granodine method handle Corp.).

Opaque mineral films (oxides and/or phosphates) with remainder porosity develop, so that a thermal oxidizing is possible.

(3) Enamelling procedure (see. z. B. A. Petzold, H. Pöschmann, email and enamelling technology, German publishing house for basic industry 1992).

Enamelling procedures lead to compact, chemical-resistant and gas-tight coatings with typical layer thickness across 50 μ M. These wise however subsequent disadvantages up:

- The production of the enamel layers requires a mehrschrittige technology with z. T. high temperatures (production of the glass frit with up to 1200 DEG C) and many component systems of high purity (typically 5 or more components).
- Enamelling coats on aluminium require additionally the element of heavy metal compounds (predominant lead oxides) to the reduction of the burning temperature or for detention switching (z. B. Vanadium oxides, Kobaltoxid).
- Enamelling are covering opak or.
- Enamel layers increase the dimensions coating sample test specimen (small accuracy to size).
- Under partial crystallinity and cracking develop layers high surface roughness, which get dirty easily.

Desired therefore means increasingly become the oxidation protection, which lead simple manageably and multi-valence more insertable to transparent and resistant coatings.

Furthermore it is the Sol geltechnique known, which in particular the production of thin anticorrosion coatings on metals allowed (see. M. Guglielmi, ?sol gel of coating on Metals?, J. Sol gel Sci. Technol. 1997, (8), 443-449, DE 197 14 949 A1). However the prior art systems do not guarantee effective contactor against thermal oxidation above 400 DEG C. In purely inorganic metallic oxide (including silicon dioxide) or metal oxide/boron oxide coatings tear arises. Organic modified Sol gellayers become with temperatures between 400. . . 500 DEG C pyrolysiert.

Another favourable application on base the Sol gels chemistry is it to use systems from phosphorus connections and nano-disperse silicic acid than phosphatization solutions or chromating replacement (z. B. US 4435219, US 5902645), in order to reach a corrosion protection at ambient temperature or to improve the adhesion of subsequent layers (lacquers). These solutions do not lead however due to the heterogeneous and part-crystalline layer character to the contactor of the surfaces before thermal oxidizing. The obtained films are porous and not scratch-proof.

The object of the invention is it, simple one which can be handled to find heavy metal-free means for the production of thin coatings on metals which lead with heat treatment above 400 DEG C to glass-like and detention-solid thin films, which prevent or reduce oxidative corrosion processes with elevated temperatures effectively. The object of the invention is it also to make a method available to the production of such means.

This object becomes by a coating composition, a coating and/or. a coating process with the features in accordance with the claims 1, 3 and/or. 11 dissolved. Favourable embodiments and practices of the invention result from the dependent claims.

Surprisingly the object could become inventive in particular by the fact dissolved that a modified phosphorus silicate gel layer on more than 400 DEG C, formed from an acidic Nanosol, becomes heated. This transparent glass-like coating to the contactor before thermal oxidation can become preferred on metals, in particular ferrous metals, aluminium, copper or their alloys used.

Article of the invention are in particular transparent coatings to the contactor before thermal oxidation, the one, annealed phosphorus silicate gel contained formed from an acidic Nanosol. Such coating layers become preferred the contactor of metals, in particular ferrous metals, aluminium, copper or their alloys used. In addition the actual known properties of oxidic phosphorus connections become,

- a) Formation glass-like melts and melting point degradation by formation of eutectics and
- b) Phosphatization and etching action in particularly favourable manner combined with one another, in order to produce glass-like and tear-free films.

The production of the inventive coating to the contactor before thermal oxidizing made in subsequent steps:

(1) Production of the acidic organophosphate Prekursor solution (I)

The production of the acidic organophosphate Prekursor solution made typically by Solvolyse three or pentavalent phosphorus connections in alcohol or alcoholic/aqueous Solvens. An acidic organophosphate solution develops. Used phosphorus connections preferably are from the type

- a) $Pm(O)_n(X)_{5m-2n}$ or
- b) $Pm(X)_3m$ $X = OR, OH, Br, Cl, I$; $m, n > 1$.

as well as their mixtures, condensation products or derivatives.

A particularly favorable variant exists in the conversion of P_2O_5 with ethanol. The solid content of the solution up to 20 Gew amounts to favourable. - % related to P_2O_5 .

Particular advantage of the organophosphate Prekursor solution is it that it can be used as catalyst for the following hydrolysis of the metallic oxide brine.

(2) Production of the coating solution (acidic Nanosol) (II)

The production of the acid phosphorus silicate nano-oil made by acid hydrolysis from metal alkoxides (inclusively silicon alkoxides) or metal halides to the corresponding brines. Typically made this process with Tetraalkoxysilanen in the acidic Prekursor solution (I).

EMI5.1

Parallel the formation of phosphorus silicates runs by condensation reaction of silicon alkoxides with phosphoric acid esters of the Prekursor solution (I). Typical inventive nano-brine (II) are water-clear solutions with solid-maintained of 2-30%. The content of P_2O_5 amounts to 5-50% related to the solid content.

The particular advantages of the so prepared coating solutions (II) are:

- in (II) the glass-formed components are homogeneous mixed
- the low flow tenacity geometry complicated by (II) the possible problem-free coating layer of substrates with
- the operational coating solutions possess an high stability in storage.

To the modification of the metallic oxide brine (and thus the coating layers) further metallic oxide Prekursoren can be added in the different process steps before the Gelbildung. The use of Prekursoren for alumina, boron oxide and/or oxides of elements III. is particularly favourable. and IV. Nebengruppe of the periodic system, like Y_2O_3 , TiO_2 and ZrO_2 . These network-formed oxides degrade the softening point of the glass-like coating layer or increase their chemical resistance and mechanical properties. In addition can towards. Metal oxides up to 20 Gew. - % (related to the solid content of (II)) are added. In addition it is possible to increase the alkali resistance of the coating layers by the additive of maximally 10% in and/or bivalent metal oxides. As particularly favourable here the additive of approx., mg or Zn-connections proved. The modification of the coating layers by towards. Metal compounds made preferably by the additive of the metal nitrates or carboxylates, which < with T; 450 DEG C thermal to be decomposed.

(3) Coat a substrate with (II)

The production thin inventive coatings made after depositing of (II) on the substrate by Aufkonzentrieren and drying process. The acidic Nanosol (II) goes into a Lyogel containing solvent (III), to further drying into the solvent-free xerogel (IV) and after annealing > 400 DEG C into a glass (V) over:

EMI6.1

The coating layer can take place via all actual usual and known coating technologies, like immersion (?dip coating?), a spraying (?spray coating?), centrifuges (?spin coating?), capers or Begiessen. Typically the layer thickness of the Xerogel layers lies within the range of 0.05. . . 2 μ M. As film bases become usual metallic substrates, in particular ferrous metals, aluminium, copper or their alloys used. Alternative one can take place the coating process on ceramic materials and/or Gläsern, in particular carbon and/or carbide materials.

Under the composition of the solution metal surfaces during the process of the coating can become etched (in the sense of a layer-formed phosphatization), so that itself the adhesive strength of the film after the heat treatment increased.

(4) Dry the layer

During and after coating the made evaporation of the solvent from the sheathing and thus a gelling (Sol gelprocess). The distance of remainder solvent and further solidification of the Xerogel film made preferably with moderate temperatures between 80 and 150 DEG C. By the inventive combination of Prekursoren typically no Phasenseparation becomes observed, so that favourable-proves transparent tear-free Xerogel films develop.

(5) Heat treatment (annealing) of the gel layer with at least 400 DEG C

The final heat treatment with $T > 400$ DEG C leads to the formation of an oxide melt, which solidifies during the cooling process glass-like. That high content at P2O5 works during the process of the annealing as melting point-degrading additive. Further progressive contributions for obtaining the melt become achieved by the small particle size and the homogeneous distribution of the components. The typically made heat treatment with temperatures of 450-600 DEG C. Dense transparent glass-like oxide coatings, which form effective contactor of metal surfaces against thermal oxidation, form.

The inventive coatings are suitable for the contactor of metal surfaces against thermal oxidation, are particularly favourably particularly the element of substrates from ferrous metals, aluminium, copper or their alloys. Further favourable applications of the coatings result in the case of the contactor of oxidation-endangered material surfaces, in particular from carbon and carbide materials as well as other particular ceramic materials.

The use of suitable compositions and technologies leads to thermal sturdy oxide coatings, which have the subsequent advantages opposite the state of the art:

- The inventive coating layers result in thin, transparent, smooth and gas-tight protective layers on different substrates
- The thermal oxidizing of the coated surface is effectively prevented.
- The coating layers cling to very good on different substrates; they are thermal stably (at least to 600 DEG C), physiologically without heistation and show an high chemical resistance, scratching firmness and an hardness.
- The coating layers are simple producible, storable and possess economic and ecological advantages (simple, environmentalcompatible raw materials and technology).
- Can be used to the coating layer of substrates of complex geometry in the painting technology usual methods problem-free. By the small layer thickness a large accuracy to size becomes achieved.

Thus in particular the subsequent favourable application possibilities result:

- Contactor of metal surfaces before thermal oxidizing and before material damages due to superheating and chemical corrosion,
- Sealing from metal surfaces to the contactor against atmospheric attack,
- Application of the inventive coating layers in the decorative range
- Application of the inventive coating layers as non-adhesive layer and surface sealing on Emailen,
- Oxidation protection of non-metallic materials, in particular of carbon fibers and carbides,
- Coating layer of pipings or reservoir vessels within the drinking water range or in the medicinal sector due to the physiological safety,
- Element as mordants as well as phosphatization and chromating replacement.

Embodiments

Example 1

Production of pure phosphorus silicate brines

a) Production of an acidic organophosphate Prekursor solution

3.0 and/or. 27.0 g P2O5 become in 300 ml ethanol (absolute) under agitating dissolved. Under heat development clear solutions A form and/or. B.

Table 1

Composition of acidic organophosphate Prekursor solutions
EMI9.1

b) Production of phosphorus silicate brines

To 300 ml solution A and/or. B are added 100 ml Tetraethylorthosilikat and 50 ml waters. After 14 h agitating low viscose rayon clear brine 1A develops and/or. 1B (life > 4 weeks).

Table 2

Composition of pure phosphorus silicate brine
EMI10.1

Example 2

Production of modified phosphorus silicate brines

100 ml sol 1B becomes mixed with 9.6 ml 10%-igen aqueous ZrO2-Sols (MERCK KGaA, Darmstadt), so that a lowviscous clear sol (2A) develops.

TABLE 3

Composition of a modified phosphorus silicate sol
EMI10.2

Example 3

Production of the glassy films, mechanical check and check on chemical resistance

Dip coating (pulling speed 30 cm/min) with the coating solutions 1A, 1B or 2A on glass or high-grade steel test specimens (10 and/or. 200 cm < 2> Coating-flat) and following drying process leads to highly transparent thin films of approx. 0.5 mu m layer thickness. The films are glassed by 5-10-minütiges heating up on 500-600 DEG C and on ambient

temperature cooled (cooling rate 30 K/min).

In order to seize substrate-independent characteristics, the mechanical properties on glass substrates became evaluated. The mechanical check of the sheathings (layer thickness 1-1.4 μm) hardness became (with Nanoindenter SHIMADZU DUH-202, depth of penetration: 80-110 Nm) and resistance to wear (reciprocating Kugeltribometer, ball diameter 5 mm, movement frequency 3 cycles per second) determined.

Table 4

Mechanical properties of protective layers against thermal oxidizing
EMI11.1

A check on chemical resistance made on high-grade steel substrates with the subsequent tests:

- a) Influence from baking-oven spray with 60 DEG C (SIDOL baking-oven cleaner, Thompson GmbH)
- b) Influence from 10% citric acid at ambient temperature
- c) Test on superheated steam sterilization barness (121 DEG C, water vapour saturation, 20 min)

The subsequent resistances were proven

TABLE 5

Chemical resistance of protective layers against thermal oxidation
EMI11.2

Example 4

Check of a coated high-grade steel sample test specimen on resistance opposite thermal oxidizing

A high-grade steel sheet coated after example 3 with sol 2A (alloy 1,4301) becomes heated on 600 DEG C. While the uncoated side discoloured (yellow, later blue), only small changes become in relation to the original state observed on the coated side (see figure).

On the basis the change of gloss (reflection angle 45 DEG) the discoloration of the surface (uncoated, not heated = 100%) can become after heating up on 600 DEG C evaluated.

Table 6

Remission of a high-grade steel inspection piece after thermal oxidizing with 600 DEG C
EMI12.1

The accompanying image shows the surface of a high-grade steel of inspection piece after 45 min thermal oxidizing with 600 DEG C (link side coated, measuring bar = to 200 μm).

Example 5

Coating layer of a copper sheet and a check on resistance against thermal oxidizing

A copper sheet coated after example 3 with sol 1A becomes for 10 min on 550 DEG C heated. While the uncoated side is completely black coloured by copper oxide formation, the coated side shows only small discolorations and good layer adhesion (stable in the Tape test).

On the basis the change of gloss (reflection angle 45 DEG) the discoloration of the surface (uncoated, not heated = 100%) can become documented.

Table 6

Remission of a copper sheet after thermal oxidizing with 550 DEG C
EMI13.1